PB-228 157

COLOR REMOVAL FROM PULP MILL BLEACHERY WASTE

James Clarke, et al

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1967

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"Color Removal from Pulp Mill Bleachery Waste"

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ABSTRACT

Al^{+3} and Fe^{+3} in concentrations from 10 to 400 ppm have been used alone and in conjunction with silica and organic polyelectrolytes for removal of color from Kraft Mill first-stage bleachery waste. These studies were made over a range of pH values from 3.5 to 10. Under optimum conditions 90 per cent of the color is removed along with 30-40 per cent of the total carbon content of the waste stream. The relationship between flocculent dose and pH level for optimum color removal will be discussed in detail along with the economics of the process developed.

ACKNOWLEDGEMENT

The authors are indebted to the Department of Health, Education, and Welfare for its financial support without which this project would not have been possible.

It is hoped that the final results will be sufficiently worthwhile to justify the expense.

INTRODUCTION

With the advent of increasingly stringent regulation as to the quality of waste water which may be discarded by industrial plants, an increasing amount of emphasis has been placed on treatment of these wastes in order to remove both organic and inorganic impurities. Since the waste quality regulations will be enforced by the Federal Government, it is important to realize that in some areas where plants are located on streams of very low water flow, the enforcement of stringent quality regulations may force the shutdown of plants where economic waste treatment methods cannot be found. It is the purpose of the present paper to discuss the removal of color and total organic carbon from paper mill bleachery effluent. It is recognized that in order to allow recycle of the water, not only color, but total solids, chloride, iron, manganese, and other impurities must be reduced to a concentration range which is compatible with the production of white paper. However, the present discussion will be restricted to color removal, and the resulting total organic carbon removal by coagulation techniques. A list of the desired properties of process water for the Kraft manufacture of white paper is shown in Table 1.[1] A range of concentrations of Al^{+3} and Fe^{+3} are used in conjunction with silica and organic polyelectrolytes to study the removal of color and total organic carbon in the present investigation.

These studies were made over a range of pH values from 3.5 to 10.

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*Davis, M.W., Jr., Professor and Clarke, J., Research Assistant, University of South Carolina, Columbia, South Carolina.

[1]Thibodeaux, L.J. and Berger, H.F., National Council for Stream Improvement, Technical Bulletin No. 203, 1967.

Since it was considered advisable to study the problem using a real waste rather than a synthetic waste, the Continental Can Company of Augusta, Georgia, was chosen as a source of waste because of its relative proximity to the University of South Carolina. Although there are four bleaching stages in the Continental Can Plant with waste waters of different compositions from each stage, it was decided to use the first stage bleachery waste since this is by far the largest volume stream [3 million gallons per day]. Chlorine gas is used as a bleaching agent for a dilute pulp suspension in this stage. The waste water as obtained from Continental Can is of light yellow color due to dissolved lignin fragments of unknown structure and contains no visible colloidal matter in suspension. The visibility, of course, is a function of the difference between the index of refraction of the solution and the particle as well as the particle size. The variation of composition of this waste stream over a period of one year is shown in Table 2. It should be noted that the waste water composition is in marked contrast to the desired composition of process water as shown in Table 1. Although there are no specific standards for discharge of color at the present time, it is probable that esthetic considerations will make such standards necessary in the future.

THEORETICAL BACKGROUND

Frequent papers have appeared in the last ten years dealing with the removal of turbidity from natural waters by coagulation techniques

using positively charged +3 ions such as aluminum and iron. A large amount of work has been done in this area by A. P. Black[2,3,4,5,6,7] and associates of the University of Florida. His studies have been concerned with the determination of optimum coagulant dosages for the removal of negatively charged color colloids from natural water by microelectrophoresis techniques. These techniques involve the measurement of the mobility of the particles in an electrostatic field. The coagulant dosage which reduces the mobility of the particles to zero is often found to correspond to the optimum dosage for maximum color removal. In other words, the optimum color removal generally takes place at or near the point at which the colloid has been completely discharged (isoelectric point); and, therefore, tends to flocculate and settle more readily. The application of this technique to industrial wastes has obvious limitations since its use must be restricted to waste waters of sufficiently low conductivity (low concentrations of dissolved salts) so that charged colloidal particles will move in the electrostatic field which is applied. In the case of the present 1st stage bleachery waste there are no visible colloids present in the waste water as received. The addition of Fe^{+3} or Al^{+3} together

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[2]Black, A.P., Journal AWWA, 51, 1545 (1959).

[3]Black, A.P. and Willems, D.G., Journal AWWA, 53, 589 (1961).

[4]Black, A.P. and Smith, A.L., Journal AWWA, 54, 926 (1962).

[5]Black, A.P. Singley, J.E., Whittle, G.P., and Maulding, J.S., Journal AWWA, 55, 1347 (1963).

[6]Black, A.P. and Chen, C., Journal AWWA, 57, 354 (1965).

[7]Black, A.P. and Smith, A.L., Journal AWWA, 57 485 (1965).

with the adjustment of the solution pH to a value required to cause the formation of hydrolysis products of the metal ion produces chemical and electrostatic interaction between the hydrolysis products and certain lignin fragments. Flocculation and settling follow. More recently Matejevic[8,9] has published two theoretical papers dealing with the coagulation of silver halide sols by $Al_2(SO_4)_3$ and $Fe(NO_3)_3$ as affected by time, pH, temperature, age of the solutions, mode of preparation of the stock solutions, and ionic strength. In the case of iron, it was concluded that it is not feasible to predict the behavior with respect to coagulation because a variety of hydrolysis species such as Fe^{+3}, $Fe\ OH^{+2}$, $Fe(OH)_2^{+}$, $Fe_2(OH)^{+4}$ are formed with the amounts of each strongly dependent on pH. Black, et.al.[10] found that for the optimum removal of natural color from water the two varibles that must be controlled are pH and $Fe(SO_4)_3$ dosage. They also noted that the optimum pH for alum is higher than that for $Fe_2(SO_4)_3$, as should be expected from the fact that Fe^{+3} is a stronger acid than is Al^{+3}.

Singley, et.al.[11] found that in the pH range 3.5-4 the predominant species of iron are positively charged. Above a pH of 4 the predominant species are neutral or negatively charged such as $Fe(OH)_3$ or $Fe(OH)_4^{-}$.

In the case of aluminum, Matejevic found that the hydrolyzed

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[8]Matejevic, E. and Stryker, L.J., J. Colloid and Interface Sci., 22, 68 (1966).

[9]Matejevic, E. and Janauer, G.E., J. Colloid and Interface Sci., 21, 197 (1966).

[10]Black, A.P. and Willems, D.G., Journal AWWA, 53, 589,(1961).

[11]Singley, J.E. and Black, A.P., Journal AWWA, 59, 1549 (1967).

aluminum ions behave in a manner consistent with the formula $Al_8(OH)_{20}^{+4}$ at pH ≈ 5.2 which is close to the optimum flocculation point. It was concluded that while mobility measurements were helpful in the interpretation of coagulation and stability phenomena, turbidity determinations were more useful in the establishment of the actual conditions of sol stability. In Matejevic's work the coagulation and reversal of charge of the colloid were followed using electrophoresis techniques. It should be noted here that there are often two different pH's at which a mobility of zero can be obtained and one of these is significantly better than the other for color removal.

Recently the technique of colloid titration for the determination of colloidal charge has been described by Kawamura.[12,13,14] The technique depends upon the assumption that a charged colloidal dispersion may be neutralized by the addition of an equivalent amount of a colloid of opposite charge. Thus, if a suitable indicator is available, colloid-colloid titrations can be carried out in much the same way as acid base titrations. Methyl glycol chitosan and polyvinyl alcohol sulfate have been found applicable as standard positive and negative colloids. Toluidene blue can be used as an indicator because it changes from blue to purple in the presence of a negative colloid.

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[12] Kawamura, S., Water and Sewage Works, Part I 114, 282 (1967).

[13] Kawamura, S., Water and Sewage Works, Part II 114, 324 (1967).

[14] Kawamura, S., Hanna, G.P., Jr. and Shumate, K.S., Journal AWWA, 59, 1003 (1967).

Kawamura notes that this technique is faster than mobility measurements, does not require specialized equipment, does not require a low salt content in the solution being examined, and can measure all colloids having ionized functional groups, regardless of size. Mobility measurements on the other hand require that the colloid be visible and that the solution conductivity be very low.

Within the last ten years increasing attention has been paid to the use of organic polyelectrolytes or colloidal silica either alone or together with inorganic salts as colloid flocculants.[15,16,17] The flocculants can be obtained in anionic, cationic, or nonionic form. In all cases they promote flocculation by linking colloidal particles by polymer bridges. The bridging phenomon is very complex being dependent on the chemical properties of the system such as pH, as well as such external variables as stirring time and intensity. Healy and La Mer[18] have shown that in general the chemical attractions between polymer and particle when acting at short distances overbalance the longer range electrostatic effects. For example, in some cases negatively charged polymers when acting on negatively charged colloidal particles induced more rapid and complete flocculation than did many positively charged polymers.

DESCRIPTION OF EQUIPMENT

All measurements of color and color removal were made with the

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[15] Black, A.P. and Christman, R.F., Journal AWWA, 53, 737 (1961).

[16] Chemical and Engineering News, 46, No. 3, 46, January 1968.

[17] Dixon, J.V., La Mer, V.K., and Linford, H.B., Journal WPCF, 39, 647, 1967.

[18] Healy, T.W. and La Mer, V.K., Journal Phys. Chem., 66, 1835, 1962.

Bausch and Lomb Spectronic 20 Colorimeter. This unit comes equipped with a 1/2 inch test tube adapter and can be quickly changed to use 3/4 or 1 inch test tubes.

Full scale deflection can be obtained over the minimum wavelength range of 340 to 625 millimicrons. The nominal band width is only 20 millimicrons and is constant over the entire wavelength range. In accordance with standard procedures[19] the measurements of color removal are carried out at 420 millimicrons corresponding to a visual color which is complementary to that of the solution. That is a violet filter is used for a yellow solution. The color is measured in Pt-Co units for which a solution made up of 1.246 gms of potassium chloroplatinate and 1.0 gms of cobaltous chloride in 100 ml. of concentrated hydrochloric acid and diluted to 1.0 liter with distilled water has as assigned color value of 500 Pt-Co color units.

The total organic carbon content of the solutions tested was measured by a Beckman Carbonaceous Analyzer. This converts the organic carbon to CO_2 and measures the infrared peak height against a standard. Evaluation may be made rapidly (2 minutes) and accurately ($\pm$ 1%) with samples containing as little as 2 mg/l of organic material.

A Bausch and Lomb dark field ultramicroscope with a Briggs cell was used to measure the mobility of colloidal particles.

A Jackson candle turbidimeter was used to measure the solution turbidity. A minimum value of 25 units is the lowest measurable turbidity by this technique.

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[19] Standard Methods for the Examination of Water and Wastewater, 12th Edition, 1965.

A Beckman Zeromatic II pH meter with a calomel reference electrode and a silver-silver chloride standard electrode was used to measure the pH.

EXPERIMENTAL PROCEDURES

A. Flocculation

(1) $AlCl_3 + Ca(OH)_2$

Preparation of saturated $Ca(OH)_2$. Place excess of reagent grade $Ca(OH)_2$ in 500 cc distilled water. Stir 2 hours and filter in absence of air.

Preparation of $AlCl_3$ solution. Weigh out 3.625 g $AlCl_3 \cdot 16$ H_2O (reagent grade) and dissolve in distilled water in a 100 ml volumetric flask filled to mark. Filter through 0.22 micron millipore filter until no Tyndall beam shows. Concentration of $AlCl_3$ is approximately 11. mg/ml.

Flocculation Procedure

a. Pipet 100 ml of filtered (Whatman #42) bleachery waste solution into a 250 ml beaker.
b. Add the desired dosage of $AlCl_3$ solution with stirring.
c. Adjust pH with saturated $Ca(OH)_2$ solution to the desired level.
d. Add demineralized water to give specified $AlCl_3$ dosage.
e. Polyelectrolytes or silica are added at this point if used.
f. Stir rapidly with magnetic stirrer for 2 minutes.
g. Record solution temperature and pH. Let sit for 1 hour. Filter through Whatman #42 filter paper. Measure pH, color, and total carbon content of solution.

(2) $Al_2(SO_4)_3$ + NaOH

Preparation standard solution of NaOH. (approximately o.1N) using reagent grade NaOH and demineralized water.

Preparation of Alum solution. Weigh out approximately 2.00 gms of $Al_2(SO_4)_3 \cdot 18\ H_2O$ (reagent grade) and dissolve in distilled water in a 100 ml volumetric flask filled to mark. Filter through 0.22 micron millipore until no Tyndall beam shows. Concentration of alum is approximately 10 mg/ml.

Flocculation Procedure

a. Pipet 100 ml of filtered (Whatman #42) bleachery waste solution into a 250 ml beaker.
b. Add the desired dosage of alum with stirring.
c. Adjust pH with o.1N NaOH to the desired level.
d. Add demineralized water to give specified alum dosage.
e. Polyelectrolytes or silica are added at this point if used.
f. Stir rapidly with magnetic stirrer for 1 minute, then slowly for 4 minutes.
g. Record solution temperature and pH. Let sit approximately 20 hours. Measure pH, color, and total carbon content of solution after decantation from settled floc.

B. Determination of Chloride Ion

This colorimetric method was developed by R. J. Bertolacini and J. E. Barney.[20,21] It utilizes mercuric chloranilate to determine chloride in the 0.05-75 ppm range. It is rapid and can be used

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[20] Barney, J.E. II and Bertolacini, R.J., Anal. Chem., 29,1187 (1957).

[21] Bertolacini, R.J. and Barney, J.E. II, Anal. Chem. 30, 202 (1958).

to detect as little as 0.2 ppm of chloride when the visible absorption peak at 530 millimicrons is used. Beer's law is followed up to at least 400 ppm of chloride. Interfering cations with the % error produced by 250 ppm of cation on the determination of 24 ppm Cl^- are as follows:

Al^{+3}, 3%, Ba^{+2}, 6%, Cd^{+2}, 8%, Cu^{+2}, 32%, Fe^{+2}, 100%, K^{+1}, 2%, Mg^{+2}, 6%, Na^{+1}, 1%, NH_4^+, 0%, Pd^{+2}, 100%, and Zn^{+2}, 37%

C. Other Analytical Determinations

All other analytical techniques such as those for determination of Fe, Mn, hardness, total alkalinity, etc. were determined by techniques described in "Standard Methods for the Examination of Water and Wastewater."

D. Sampling and Data Taking

The samples of waste water were obtained in 5 gallon polyethyene bottles. It was noted that a colored flocculent sediment accumulated in the bottom of these bottles over a period of several weeks. After filtering it was noted that further accumulation took place with the passage of time.

The data for a particular waste were normally taken over a period of several months. This introduced some variation into the data due to the removal of organic material by sedimentation.

DISCUSSION OF EXPERIMENTAL RESULTS

The curves of absorbance vs. wavelength at various pH's shown in Figure 1 and 2 are typical of yellow solutions of naturally occurring organic color which have been previously reported by Black

and Christman?[22] The continual decrease of absorbance from 340 up to 625 millimicrons indicate organic molecules which absorb strongly in the ultraviolet with a tail extending into the visible region. The strong absorption in the complementary color region (violet) makes the solution appear yellow in color. The increase in color with pH is believed to be related to the oxidation of lignin or its fragments to a quinonoid structure of the quinonemethide type.[23]

From Table No. 2 it can be seen that the colored material is of larger size than the average of the total carbon (TC) since 58-72% passed a 10 mu Millipore filter while 87-96% of the TC passed the same filter. It should also be noted that the sample obtained in June, 1967 contained substantially larger color molecules than the other three samples shown in Table 2 and was also treated with less chlorine. Thus chlorine evidently breaks down the size of the color molecules as would be expected. It would, therefore, appear that the comparison of different bleachery wastes can only be meaningful if the source and history is known.

The removal of both TC and color by $Al_2(SO_4)_3$ and $AlCl_3$ is optimum at a pH $\cong$ 5.3. Both salts show a removal of 80% of the color and 30% of the TC as shown in Figures 3 and 4.

The use of $AlCl_3$ is more effective than alum in the removal of color from bleachery waste. On a mole basis only 1/2 the amount of Al^{+3} as $AlCl_3$ is required to remove 80% of the color

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[22]Black, A.P. and Christman, R.F., Journal AWWA, 59, 753 (1963).

[23]"Lignin Structure and Reactions", Advances in Chemistry, Series 59 (1966).

when compared with alum. The optimum dosage for $AlCl_3$ is 110 mg/liter. The difference in performance of these two aluminum salts may well be connected with the use of $Ca(OH)_2$ for pH adjustments of the $AlCl_3$ solution as compared with NaOH for pH adjustment of the $Al_2(SO_4)_3$ solution. The Ca^{+2} should aid the Al^{+3} in flocculating the color colloids since its concentration is about three times as great even though it is not as effective as a coagulant due to its lower charge. Very little difference between $AlCl_3$ and alum is noted in TC removal. Since the TC molecules have been shown to be much smaller than the color molecules, they may be in true solution and thus not behave as the color molecules. These results are shown in Figure 5.

The addition of silica to $AlCl_3$ as an aid to flocculation does not significantly improve the removal of color or TC as shown in Figure 6.

The effect of polyelectrolytes on TC and color removal in combination with $AlCl_3$ is shown in Figure 7. The polyelectrolytes were manufactured by the Dow Chemical Company and include all three classes: 0.9 ppm anionic (A-21), 1 ppm cationic (C-31), and 4 ppm nonionic (N-17). These concentrations were determined by a study of polyelectrolyte dose vs. TC and color removal at an $AlCl_3$ concentration of 110-112 mg/liter. No increase in either TC or color was obtained although improved settling did result.

A study of agitation times up to 1 hour on TC and color removal in the presence of 2 mg/liter of silica as a flocculating aid is shown in Figure 8. The study indicates some improvement in color removal to 90% but little change in TC removal (to 31%). The agitation was

by magnetic stirrer at as slow a speed as consistent with constant stirring.

A study of the effect if $Fe_2(SO_4)_3$ dosage and pH on TC and color removal is shown in Figures 9 and 10. However, color and TC removal increase with dosage over the concentration range studied, making the optimum dosage an economic decision. The optimum pH for TC removal (4.5) is somewhat higher than that for color removal at the same salt dosage. The peculiar shape of the color vs. dosage curve at pH = 5.25 in Figure 9 is caused by turbidity in the solution giving falsely high color indications.

Economics of Waste Treatment

The chemical costs for the treatment at a dosage of 110 ppm of $AlCl_3$ plus pH adjustment by $Ca(OH)_2$ will be about 7.7 cents per 1000 gallons. No recovery of chemicals is assumed. The price of 100% $AlCl_3$ is taken as 5.25 cents per pound. Cost of $Ca(OH)_2$ is estimated at 1 cent per pound. Cost data for $AlCl_3$ is taken from the Oil, Paint, and Drug Reporter.

The chemical dosts for treatment with alum at a dosage of 140 ppm is 2.5 cents per 1000 gallons without including the cost of NaOH.

For $Fe_2(SO_4)_3$ treatment at a dosage of 200 ppm the cost per 1000 gallons will range from 1.5 to 3.0 cents depending on cost of $Fe_2(SO_4)_3$ without including the cost of NaOH. The cost of NaOH treatment will depend on costs of various strengths of NaOH solutions. If a cost of 3.0 cents per pound of NaOH is assumed, the cost of pH adjustment will be about 10 cents per 1000 gallons for either alum or $Fe_2(SO_4)_3$ neutralization.

Therefore, it appears that the process involving neutralization with $Ca(OH)_2$ is the most economic one studied thus far.

CONCLUSIONS

From the present data it is concluded that the optimum pH for TC and color removal by $Fe_2(SO_4)_3$ is 3.8 versus 5.3 for $AlCl_3$ and alum. This is consistent with the theory that positively charged metal hydroxide complexes which form at these pH's are of prime importance in coagulation phenomena.

The optimum dosage of $AlCl_3$ is about 100-110 mg/liter while that for alum and $Fe_2(SO_4)_3$ will be determined by economics since the removal increases slowly with dosage rate. Neither silica nor the organic polyelectrolytes have any significant effect on TC or color removal but do tend to promote better flocculation.

Stirring time up to 30 minutes caused an increase in color removal to 90%. In the presence of 2 mg/liter of silica the data seemed more reproducible probably due to better settling and, therefore, less turbidity.

The most economic process studied here involves the use of $AlCl_3$ as coagulant with $Ca(OH)_2$ for pH adjustment. For removal of 80 - 90% of the color and 30% of the total carbon, a cost of 7.7 cents per 1000 gallons is estimated.

TABLE NO. 1

Ranges of Desired Properties of Process Water For Kraft Manufacture

	Bleached Paper
pH	6.8-7.3
Solution Color (Pt-Co)	0-5
Chloride, ppm	10-150
Total Alkalinity, ppm	20-75
Hardness, ppm $CaCO_3$	5-100
Dissolved solids, ppm	50-250
Fe, ppm	0.2
Mn, ppm	0.1
Chemical Oxygen Demand	0-8
Turbidity, ppm	0-5
Biochemical Oxygen Demand	0-2

TABLE NO. 2

1st. Stage Bleachery Waste Analyses

	8-10-66	12-8-66	6-1-67	8-1-67
Conductance, mho's (22°C) x 10^{+6}	4800	4090	1875	4830
pH	2.21	2.21	2.50	2.19
Solution Color (420mu) Pt-Co units	320	406	217	462
Solution Color passing 220 mu filter	261(81.5%)	337(83%)	150(69%)	398(86.2%)
Total Carbon passing 220 mu filter	—	—	—	94%
Solution Color passing 10 mu filter	230(71.8%)	253(62.4%)	92(42.4%)	270(58.4%)
Total Carbon passing 10 mu filter		96.4%		87%
Chloride, mg/l	608	620	294	616
Total Carbon, mg/l	90.2	106.5	80	135
Sodium, mg/l	112.6	52.4	47.7	—
Hardness, mg/l $CaCO_3$	87.8	178.2	110	204
Acidity, mg/l $CaCO_3$ (phenolphthalein)	684	512	241	1198
Turbidity, units (filtered through Whatman #42)	<25	<25	<25	<25
Fe, mg/l	3.46	2.2	0.74	—
Residue on drying at 105°C, mg/l	350	460	430	760

Figure 1. ABSORBANCE OF BLEACHERY WASTE AS A FUNCTION OF WAVELENGTH AND pH

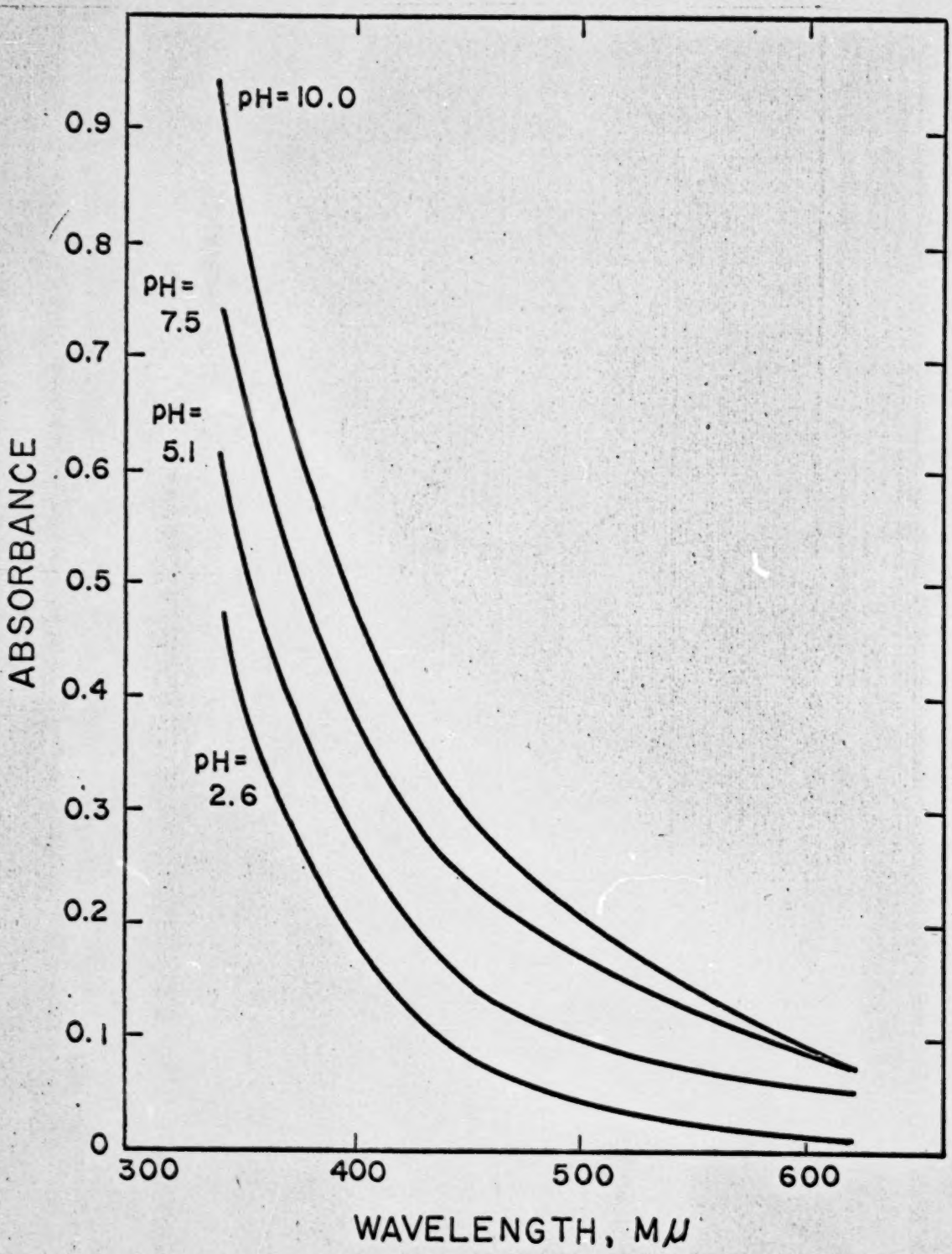

Figure 2. EFFECT OF pH ON BLEACHERY WASTE COLOR AT 420 Mu

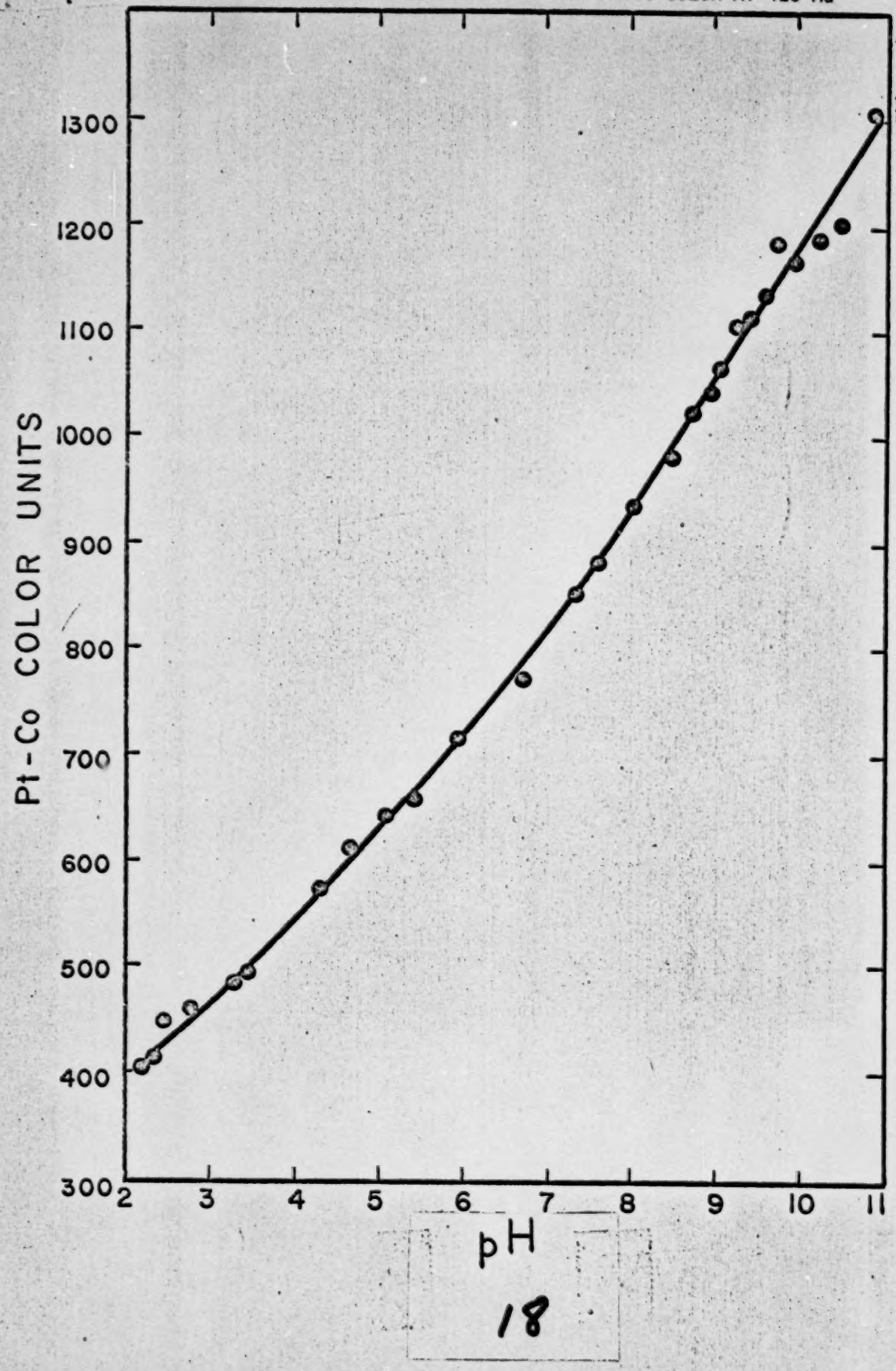

Figure 3. EFFECT OF pH ON COLOR AND TOTAL CARBON REMOVAL BY $AlCl_3$

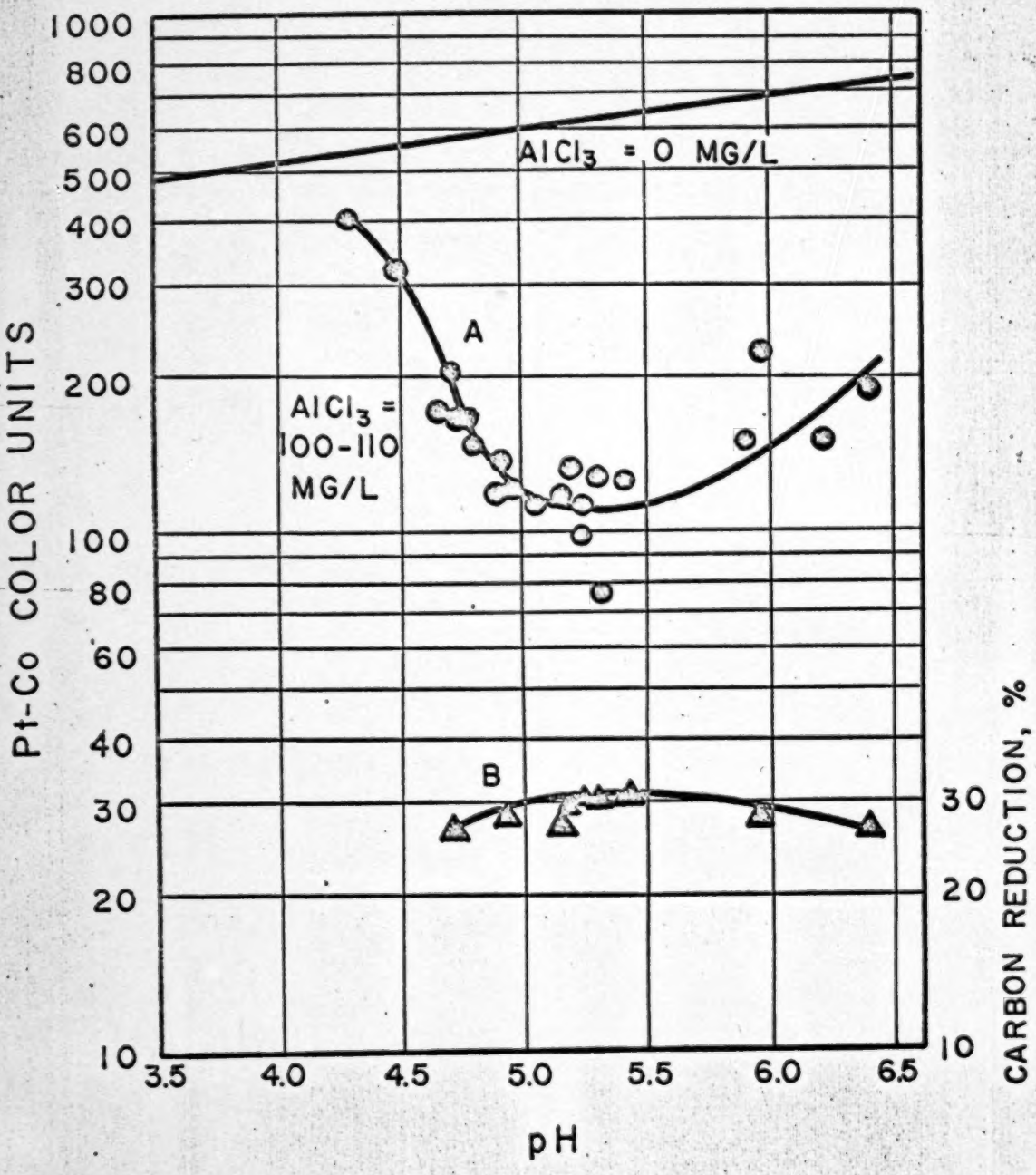

Figure 4. EFFECT OF pH ON COLOR AND TOTAL CARBON REMOVAL BY ALUM

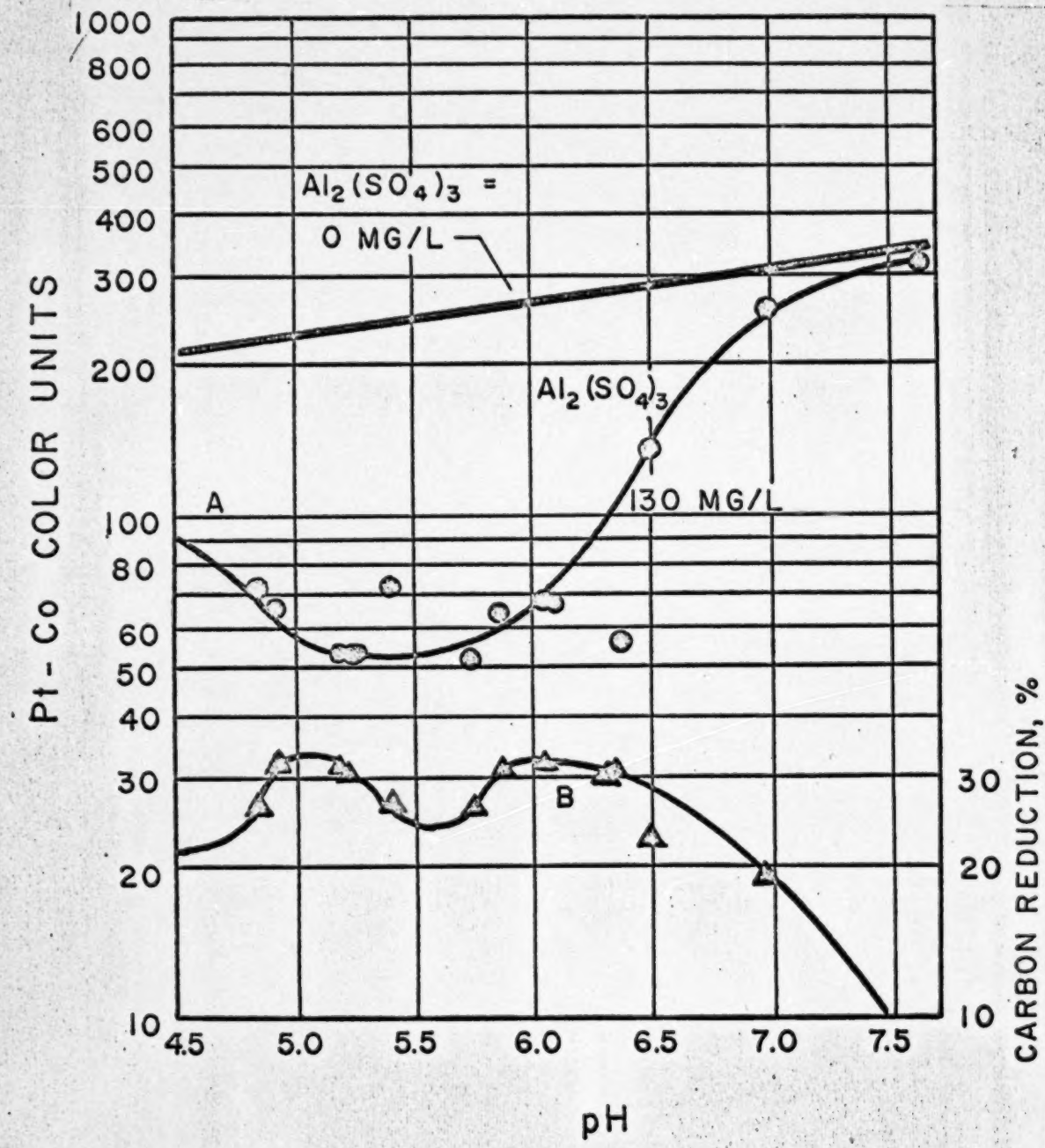

Figure 5. EFFECT OF ALUMINUM SALT DOSAGE ON COLOR AND TOTAL CARBON REMOVAL AT pH OF 5.2

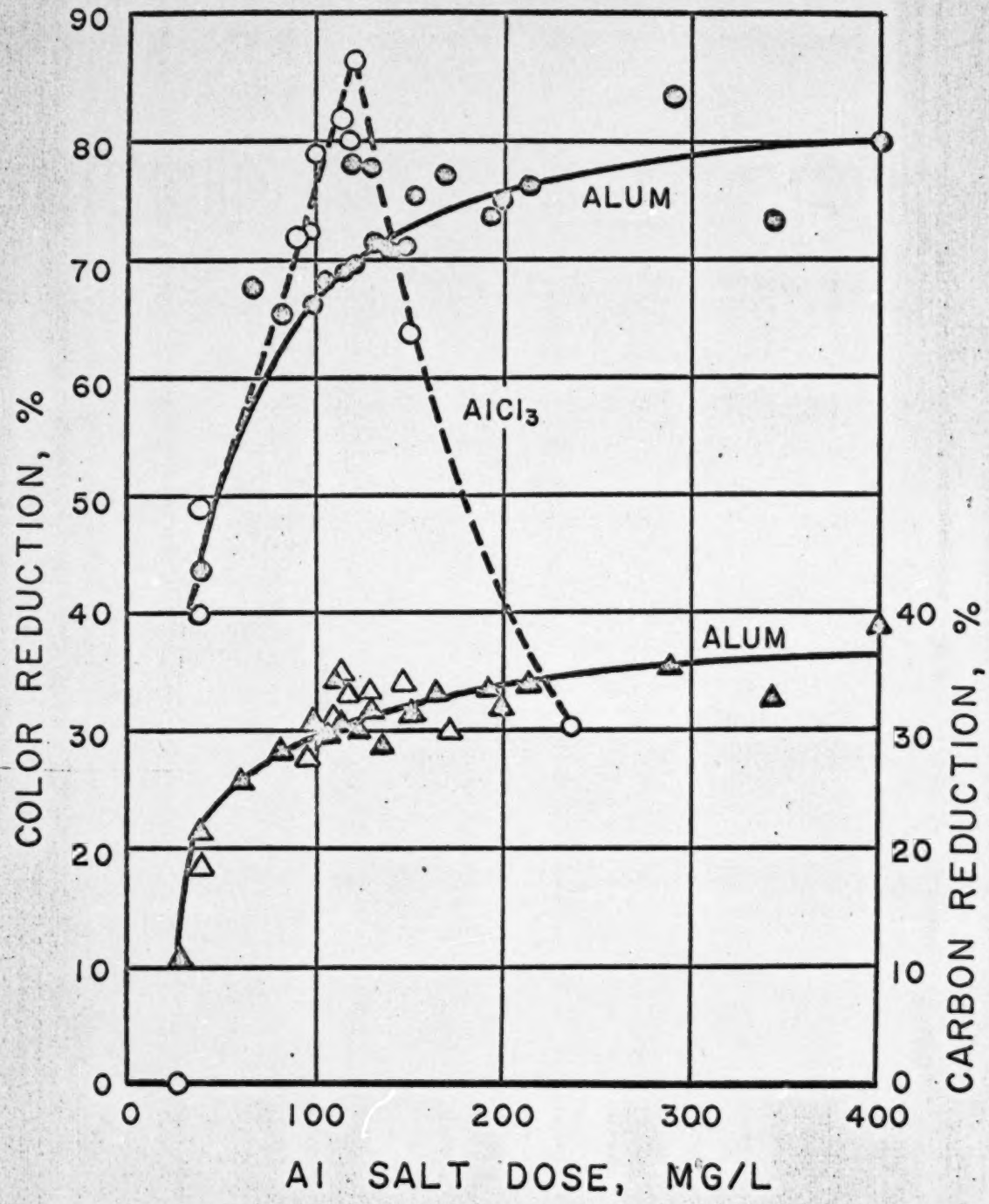

Figure 6. EFFECT OF SILICA ON THE REMOVAL OF COLOR AND TOTAL CARBON BY $AlCl_3$ AT pH OF 5.3 - 6.1

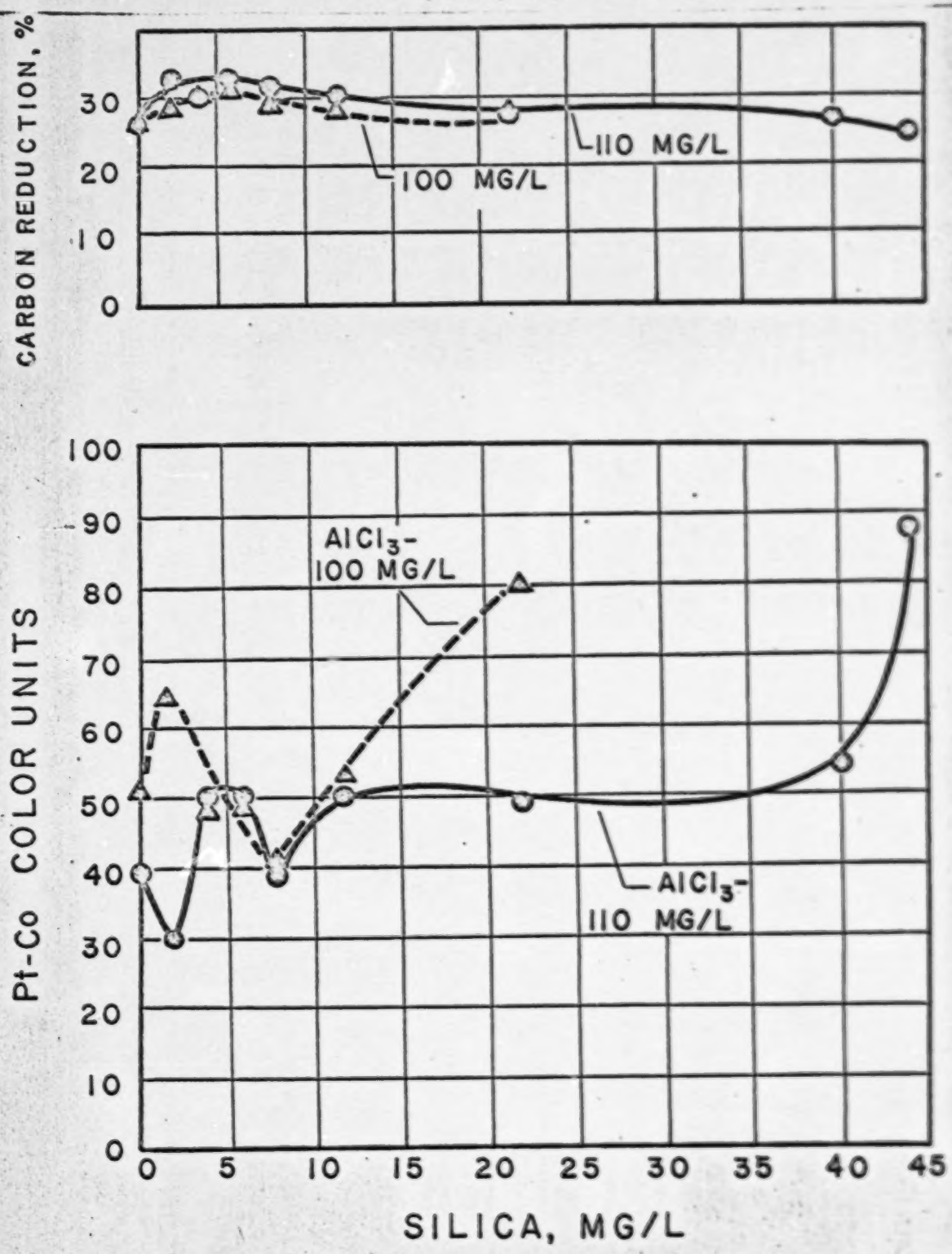

Figure 7. EFFECT OF POLYELECTROLYTES ON THE REMOVAL OF COLOR AND TOTAL CARBON BY $AlCl_3$ AT pH OF 5.3

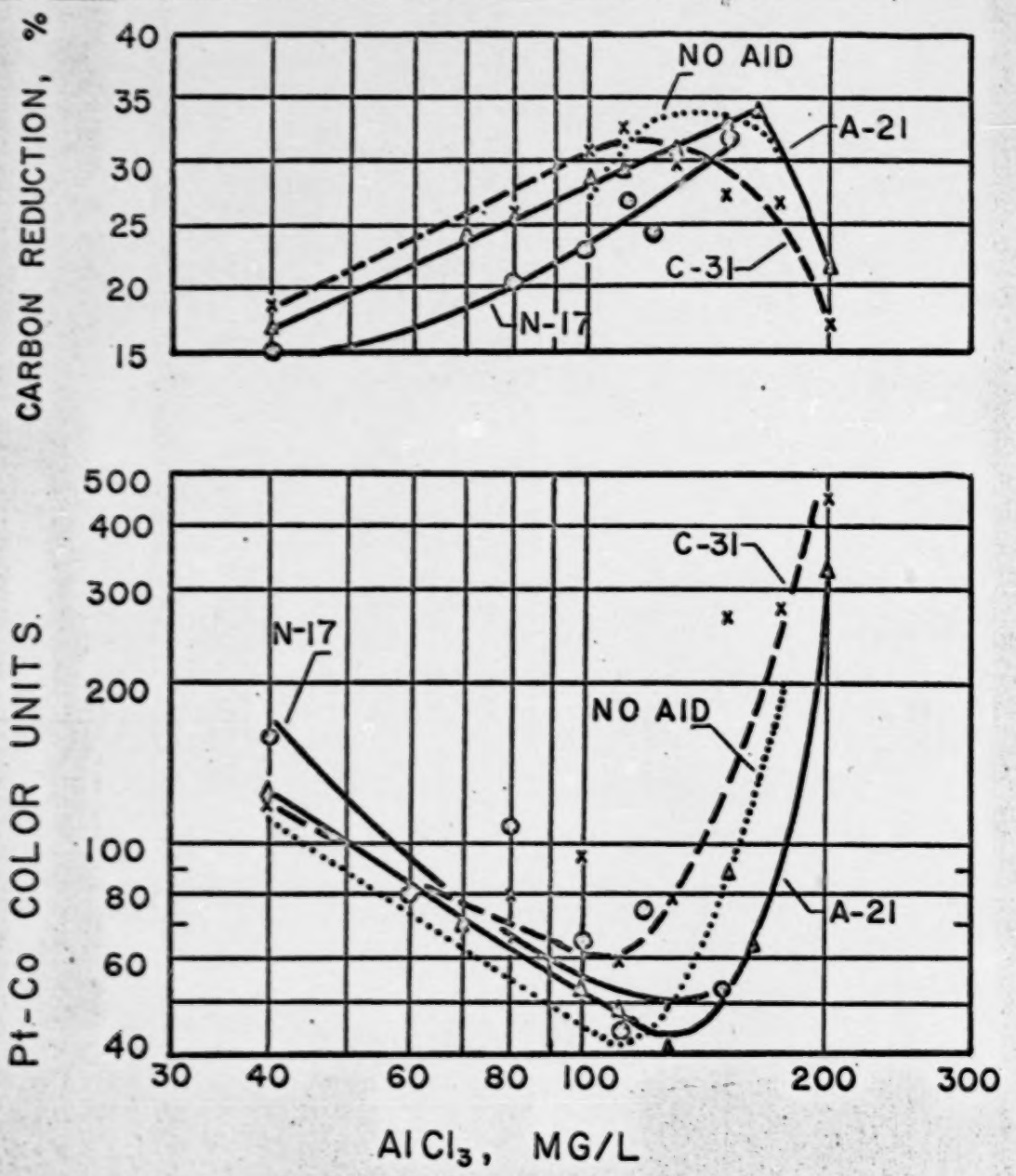

Figure 8. THE EFFECT OF AGITATION TIME ON COLOR AND TOTAL CARBON REMOVAL IN THE PRESENCE OF SILICA AT 112 MG/L OF $AlCl_3$, pH = 5.3

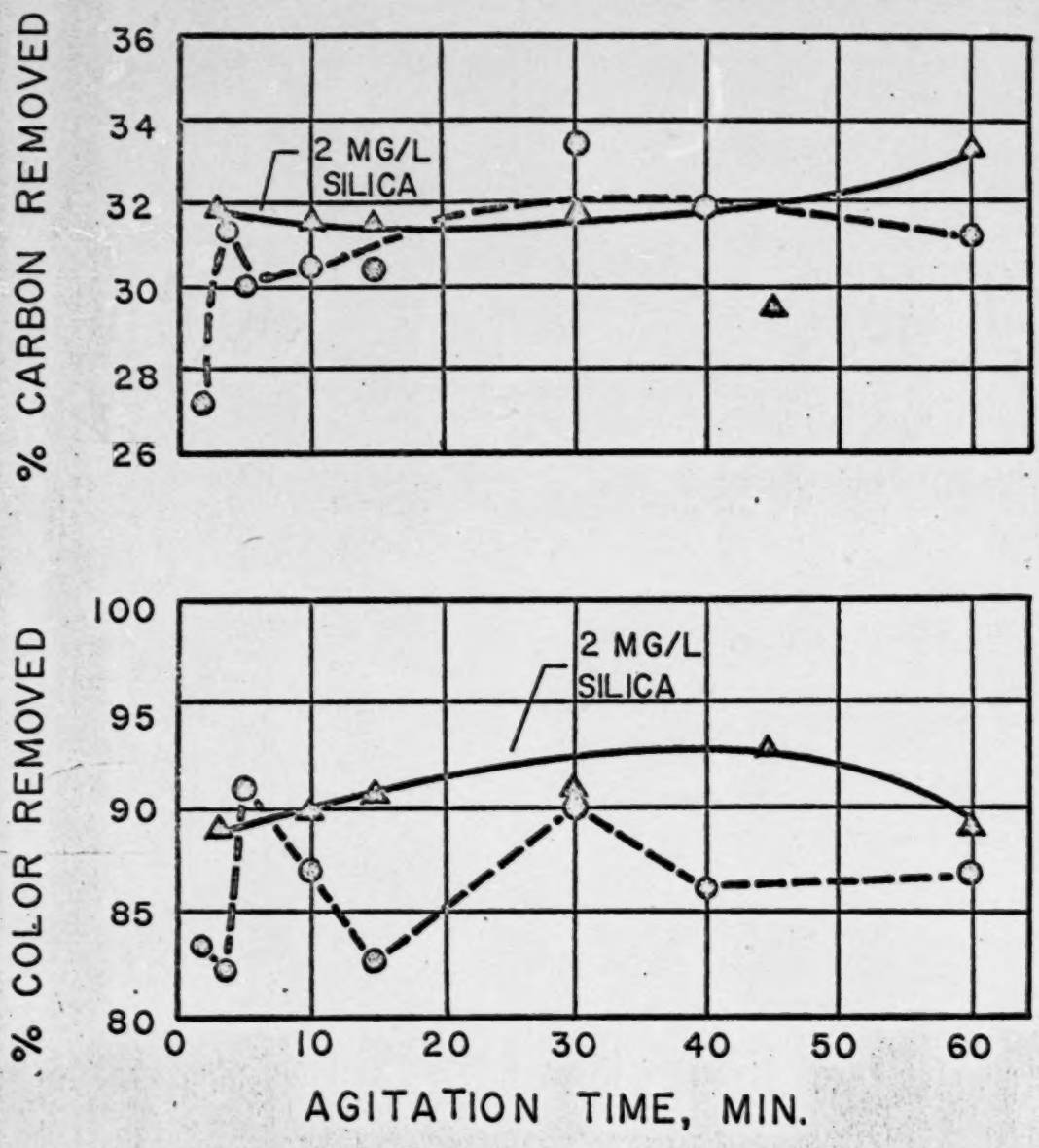

Figure 9. EFFECT OF $Fe_2(SO_4)_3$ DOSAGE AND pH ON COLOR AND TOTAL CARBON REMOVAL

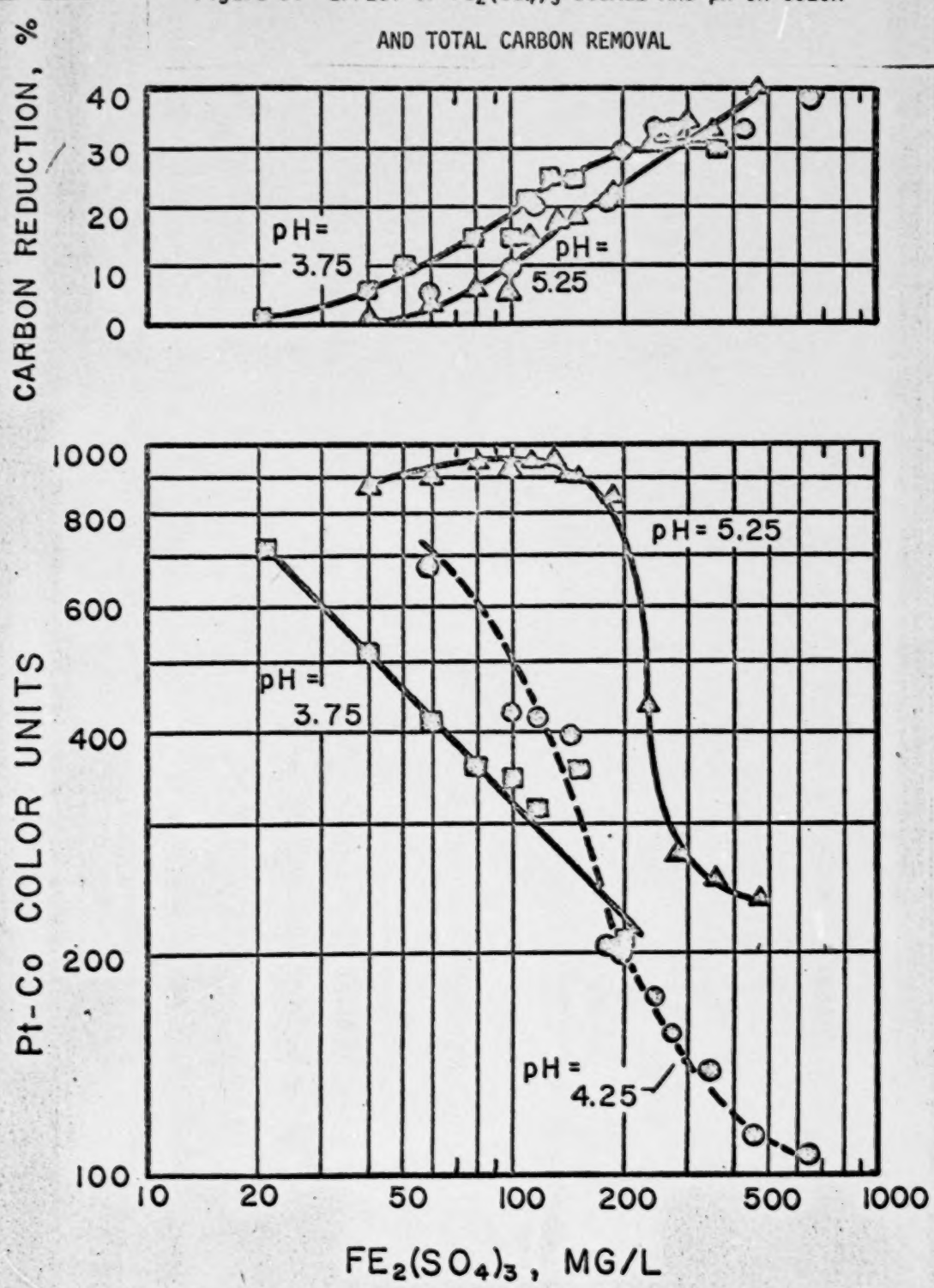

Figure 10. THE EFFECT OF pH ON COLOR AND TOTAL CARBON REMOVAL BY $Fe_2(SO_4)_3$ AT ● 97 AND ▲ 140 MG/L